Monocyclic (CH)_n—A Heilbronner Möbius Aromatic System Revealed**

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Dedicated to Professor Edgar Heilbronner

In 1964 Heilbronner predicted that singlet [4n]annulenes would be aromatic systems in twisted conformations where the p orbitals lie on the surface of a Möbius strip (Figure 1).[3]

Although the Möbius concept has been employed extensively to interpret reactions and bonding,[2,3] Möbius annulenes conforming to Heilbronner’s original idea have still not been reported. Heilbronner pointed out that rings with twenty atoms or more might adopt Möbius geometries “without any apparent angle or steric repulsion strain”. However, we have discovered computationally that Möbius aromaticity is possible in a much smaller ring system, namely, the cyclononatetraenyl cation. Judging from early experimental evidence,[4,5] this species may actually have been encountered more than once almost three decades ago!

A monocyclic (CH)_n cation of unspecified nature, but which allowed isotope label scrambling, was first postulated in 1971 as a short-lived intermediate in the solvolysis of exo-9-chlorobicyclo[6.1.0]nona-2,4,6-triene in aqueous acetone at 75 °C.[5] The reactant containing deuterium at C9 (Scheme 1) gave a bicyclic product, cis-8,9-dihydroindene-1-ol (3, X = OH), with uniformly distributed deuterium label.[6] Shortly afterwards Anastassiou and Yakulj succeeded in preparing 9-halocyclononatetraene (2, stereochemistry under-determined).[7] Under ionizing conditions (liquid SO_2 at −66 °C), D-labeled 2 gave 3 (X = Cl) by ion-pair return, again with complete statistical distribution of the label (1/9D per C atom).[8]
In view of the expected antiaromaticity of the planar cyclononatetraenyl cation, Anastassiou and Yakali wondered why the ion forms so easily and how the positions could become equivalent.\textsuperscript{15} They represented (CH)\textsubscript{4} in a coiled conformation (4 in Figure 2, structure on the right),\textsuperscript{16} which was felt to be “incapable of skeletal inversion without experiencing again the adverse effects of antiaromaticity.”\textsuperscript{15} We now report computational evidence that the eight-membered cation forms so easily and how the positions could become equivalent.\textsuperscript{15} They represented (CH)\textsubscript{4} with paramagnetic susceptibility exaltations of 8.5. The diamagnetic susceptibility of electron monocyclic cation (CH)\textsubscript{4} is in accord with the experimentally estimated half-life of 4 (\tau\textsubscript{1/2} < 10 min at \(-66^\circ C\) in liquid SO\textsubscript{2}).\textsuperscript{15-17} Although modest in magnitude, the aromaticity of transition state 8 (NICS = \(-6.0, A = -7.0\) ppm cgs; Table 1) is as expected for a pericyclic transition state.\textsuperscript{15} The bicyclic C\textsubscript{s}-symmetric 1,4-}

![Scheme 1. Reaction of deuterated 1 and 2 to the dihydroindenones 3 with complete statistical distribution of the label.](Image)

![Figure 2. Conformations of (CH)\textsubscript{4}: The Möbius conformation 4 (C\textsubscript{4}) and the strongly bond alternating form 5 (C\textsubscript{5}); the planar antiaromatic singlet 6 (C\textsubscript{6}); 7 and 8 are transition states for enantiotomerization and disrotatory ring closure of 4, respectively. The latter connects to the bicyclicbishomoaromatic 9 (C\textsubscript{9}). For further details, see text.](Image)

Table 1. Relative energies \(E_{\text{rel}}\) [kcal mol\(^{-1}\)] at the B3LYP/6-311+G** and CCSD(T)//B3LYP/6-311+G** level, NICS [ppm], maximum differences in C–C bond lengths \(\Delta R_{C-C}\) [Å], magnetic susceptibilities \(\chi\) and diamagnetic susceptibility exaltations \(\Delta \chi\) [ppm cgs] of singlet (CH)\textsubscript{4} species.

<table>
<thead>
<tr>
<th>Species</th>
<th>NIMAG\textsuperscript{[a]}</th>
<th>(E_{\text{rel}})</th>
<th>ZPE</th>
<th>NICS\textsuperscript{[b]}</th>
<th>(\Delta R_{C-C})</th>
<th>(\chi\textsuperscript{[c]})</th>
<th>(\Delta \chi\textsuperscript{[c]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. (C\textsubscript{2})</td>
<td>0</td>
<td>0.0</td>
<td>94.4</td>
<td>-13.4</td>
<td>0.043</td>
<td>-67.7</td>
<td>-18.8</td>
</tr>
<tr>
<td>5. (C\textsubscript{5})</td>
<td>0</td>
<td>21.6</td>
<td>94.3</td>
<td>+8.6</td>
<td>0.128</td>
<td>-30.8</td>
<td>+18.1</td>
</tr>
<tr>
<td>6. (C\textsubscript{6})</td>
<td>2</td>
<td>26.3</td>
<td>93.6</td>
<td>+42.0</td>
<td>0.131</td>
<td>+63.6</td>
<td>+112.2</td>
</tr>
<tr>
<td>7. (C\textsubscript{7})</td>
<td>1</td>
<td>+0.9</td>
<td>94.1</td>
<td>-0.9</td>
<td>0.146</td>
<td>-48.9</td>
<td>0.0</td>
</tr>
<tr>
<td>8. (C\textsubscript{8})</td>
<td>1</td>
<td>+8.1</td>
<td>93.9</td>
<td>-6.0</td>
<td>0.139</td>
<td>-55.9</td>
<td>-7.0</td>
</tr>
<tr>
<td>9. (C\textsubscript{9})</td>
<td>0</td>
<td>-16.6</td>
<td>95.9</td>
<td>-11.8</td>
<td>-0.067</td>
<td>-67.4</td>
<td>-18.5</td>
</tr>
</tbody>
</table>

\[\textsuperscript{[a]}\]Vibrational analysis at the B3LYP/6-31G** level. \[\textsuperscript{[b]}\]GIAO method in G94. \[\textsuperscript{[c]}\]At the RHF/6-31G** level. \[\textsuperscript{[d]}\]CSGT method in G94. \[\textsuperscript{[e]}\]Relative to +8.1. \[\textsuperscript{[f]}\]Energy at the CCSD(T)//B3LYP/6-31G** level relative to 4 (including ZPE corrections at the B3LYP/6-31G** level)

bismothromtropylum cation 9 (16.6 kca/mol^1 more stable than 4), was confirmed to be bishomoaromatic by Cremer based on geometric and magnetic criteria.[15] The NICS at the geometric center of 9 (−11.8) and A = −18.5 ppm cgs (i.e., similar to that of 4[16]), corroborate this conclusion. This cation reacts to give the observed cis-8,9-dihydroindenes 3 (X = OH or Cl).[4,5]

In summary, the geometric and magnetic criteria (NICS and A) exhibited by 4 now reveal this species to be the first Möbius aromatic system in the Heilbronner sense, for which there is experimental evidence.[4,5] Without such evidence, the nature of 4 was not recognized originally. Furthermore, early speculations were incorrect: While conformation scrambling of the deuterium label, observed for transition state 7 is not high in energy,[18] the complete scrambling of the deuteron label, observed for 3 even at −66 °C, is consistent with the low barrier computed for 7, permitting rapid interconversion of the helical 4 enantiomers. Ninefold repetition of the enantiomerization results in complete distribution of a deuteron label in 4. In conclusion, the experimental findings reported nearly three decades ago[4,5] are explained by assuming that the (CH)^{+} cations were 4e-electron Möbius aromatic systems. Our prediction that 4 is the most stable monocyclic (CH)^{+} cation might be verified by applying modern experimental techniques such as laser flash photolysis, which has been employed to observe short-lived carbocations.[17]

Keywords: aromaticity, carbocations, density functional calculations, magnetic properties, Möbius strips

[7] We learned only recently that Anastassiou and Yakali actually considered the possibility of a Möbius cation (CH), in 1969, and this anticipation might have been also the incentive to carry out the early investigations outlined here: A. G. Anastassiou, E. Yakali, private communication (see also reference [5c]).
[9] The most stable triplet species (C) is 20.7 kcal/mol^1 higher in energy than 4 (UB3LYP/6-31G^*). Y. V. Gogonea, unpublished results.

\[
\text{Cp}^\text{**}_8\text{AlI}_6: \text{An Intermediate in Reactions Leading to Elemental Aluminum and AlIII Species?**}
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Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

As we have demonstrated in earlier work, Al^III species are reactive both in solid noble gases and under preparative synthetic conditions,[11] and often react to give thermodynamically more stable Al^II products and metallic aluminum. [Cp^2Al]^+ [Cp^2AlCl]^+ is thus formed as the final product from Cp^2Al and AlCl3 with simultaneous deposition of aluminum. This isomer of the sesquichloride [Cp^2AlCl]^+ contains the aluminocenium ion [Cp^2Al]^+ as a structural peculiarity.[15] To understand this reaction mechanism and to find out how Al^III species can react in general, we carried out investigations with the aim of capturing intermediate products of the disproportionation.

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